

Development of High Throughput Methods for Polymer Nanocomposite Research

J. W. Gilman*, R. Davis, M. Nyden, T. Kashiwagi, J. Shields, W. Demory
National Institute of Standards and Technology
100 Bureau Drive
Gaithersburg, MD 20899

Introduction

This chapter will present an overview of the development of two high throughput (HT) methods:

1) preparation of formulated polymer libraries using extrusion, 2) screening of flammability properties using flame spread measurements.

Nature and evolution are possibly the best evidence of the effectiveness of combinatorial and high throughput processes. As a research tool the high throughput concept is not only itself a *disruptive technology*, but it is likely to be the major source of new *disruptive technologies* in any field where it is applied.¹ The application of these types of concepts to the development of materials began with Hanak and coworkers at RCA in the early 1970s. Specific to the point of these first papers were the rapid processing methods for sample preparation (co-sputtering of continuum compositions), the characterization methods, and the inherent greater efficiency of Hanak's "multiple-sample concept."² Today the sample architecture that Hanak described in his original papers is referred to as "composition-spread" or "gradient" type.

For the purposes of our research we are utilizing the gradient approach and developing experimental methods which simply offer "higher throughput" or faster data generation. Of course, more data is not the final goal, we strive for the opportunity to more completely explore

the nearly unlimited number of ideas one has, with the ultimate output being the rapid generation of useful knowledge.

The focus of this research is the development of fundamental structure-property relations for polymer nanocomposites. Of primary interest are the governing mechanisms behind the enhanced mechanical properties and the improved flammability properties of nanocomposites.

Polymer nanocomposites are prepared by mixing a polymer (or monomer) with some dissimilar material, or additive, that has one or more dimensions on the nanometer scale. Over the last few decades a wide variety of materials and synthesis approaches have been developed that allow molecular-level control over the design and structure of nanocomposite materials. Nanocomposites have been prepared by sol gel methods: by *in situ* polymerization routes, and by using simple compounding methods.⁴ All of these approaches share a common theme; the intermingling, on the nanometer scale, of dissimilar materials for the purpose of creating new materials with properties not available from either of the component pure materials. For example, simple organic polymers modified with layered silicates^{5,6} have been prepared with improved heat distortion temperatures, twice the modulus, a factor of ten lower permeability to gases and solvents, improved thermal stability, a 4-fold lower flammability^{7,8,9,10,11}, enhanced ablative performance,¹² and reduced rates of degradation in space.¹³ All these attributes derive from incorporation of only 5-10 % (by mass) of the layered silicate, and only occur if the surface-area between the two phases is very high, i.e., the particle size of the additive is on the nanometer scale and the degree of phase mixing is homogeneous on the nanometer scale. In other words, the fraction of material in an “interphase” must be high. Other types of nanocomposites show similar enhanced properties as long as the same conditions are met. Polyoligosilsesquioxane, POSS, materials blended or copolymerized with various polymers, “sol-gel hybrid materials,”¹⁵ nano-silica composites, and polymer-nanocomposites based on

graphite and carbon nano-tubes, are other types of nanostructured materials with unique properties.¹⁶

One might ask why does the study of nanocomposites require the development of high throughput methods? The answer is simply that there are a large number of parameters which influence polymer-nanocomposite performance, and to develop a detailed understanding of these materials a large volume of the associated multi-dimensional property space should be investigated. The multi-dimensional parameter space for polymer-nanocomposites, shown in Table I, consists of the obvious list of different material types under consideration, such as “polymer” and “nano-additive”. All of these materials must be miscible with one another so that a nanocomposite can form, and so that there is a strong stabilizing interaction at the interphase between the two dissimilar materials. This is essential both for the phase stability of the nanocomposite, and for optimal physical properties. These requirements introduce the next parameter, “surface chemistry”. Control of surface chemistry is most often accomplished, in layered silicate nanocomposites, by modification of the inorganic surface with an organophilic reagent, such as an alkyl ammonium, or a chelating agent. In POSS materials many different functionalities can be incorporated directly into the structure. While this means that no additional “surface” treatment is required there are still a large number of possible POSS materials which need to be evaluated to obtain the optimal property improvement for a specific application.”

Table 1. Multi-dimensional Parameter Space for Polymer-Nanocomposites.

Polymer"	Nano-additive	Surface Chemistry	Processing Conditions	Conventional additives	Flame Retardant
PE	Layered-silicate	Alkylammonium	Temperature	Processing-Stabilizers	Phosphate
PP	POSS	Imidazolium	Shear	UV- Stabilizers	Halogenated
PS	Carbon-nanotubes	Chelates	Residence time	Antioxidant	Silicon Based
PA6	Silica	Silated		Fillers	
PU		Alkyl		Pigments	
PVC		Carboxylate			
PC					
PEO					
Epoxy					
		.	.		
		.	.		
~ 10	~ 10	~ 10	~ 10	~ 10	~ 10

a: polyethylene (PE), polypropylene (PP), polystyrene (PS), polyamide-6 (PA6), polyurethane (PU), polyvinyl chloride (PVC), polycarbonate(PC), polyethyleneoxide (PEO).

Like layered-silicates both carbon-nanotubes and silica nano-particles require secondary functionalization to render them miscible with polymers. This brings us to the very critical parameter, "processing conditions." The optimal processing conditions for a given nanocomposite system **will** depend on complex interactions with the previous three parameters. We have found that careful control of processing conditions is critical both to the preparation of a nanocomposites, and also to preventing degradation of the nanocomposite during processing.¹⁸ For the purpose of considering combinations of nanocomposites with other "conventional additives" one also needs to include the investigation of possible synergistic and antagonistic interactions with processing and UV stabilizers, pigments, dyes, fillers and for our particular interests, flame retardant additives. This list of parameters generates on the order of 10^6 combinations or formulations worthy of investigation. To try to study this property space high throughput methods must be developed for nanocomposites.

Experimental

Homogeneous and compositionally graded samples containing ammonium polyphosphate (**APP**) and pentaerythritol (**PER**) and/or organic modified layered silicate (OLS, dimethyl, dehydrogenated tallow ammonium montmorillonite, **15A**, from Southern Clay Products, www.nanoclay.com) in **polystyrene** (*PS*, Shell, Styron **663**) were produced in our twin screw extruder (B&P 18 mm, 25:1, L:D, feed rates (2-3) kg/h). The samples were strips (approximately 1.5m long, 7 mm wide and 2 mm thick, see Figure 1) consisting of PS blended with varying amounts of additives. In the gradient samples we attempted to create a linear concentration gradient (from $C \approx 0\%$ to $C \approx 30\%$ additive by mass) by increasing the rate of feed from the hopper containing additive linearly with time. The evaluation of the flame spread properties of the samples was carried out in our modified flooring radiant panel device (see Figure 2). The homogeneous composition samples were evaluated in a *gradient* flux environment (see Figure 4). The gradient composition samples were evaluated for flame spread under a *constant* flux of $(16.8 \pm 0.4) \text{ kW/m}^2$ in the modified flooring radiant panel device. This was accomplished by fixing the methane burner parallel to the sample holder.

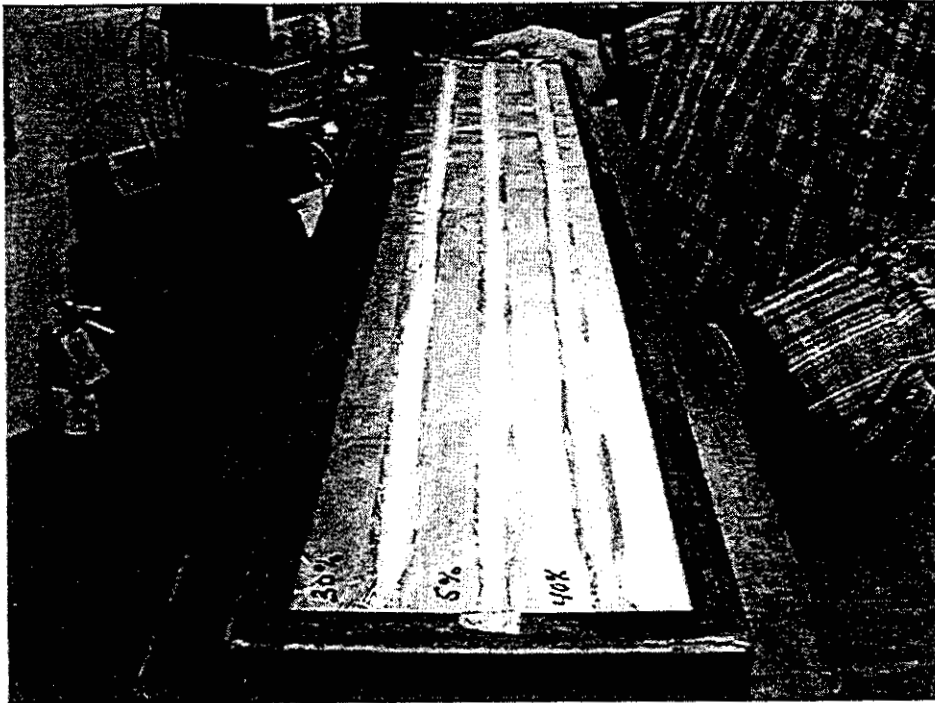


Figure 1. Extruded strips of polystyrene (PS) with various concentrations (30 %, 5 %, 40 %) of a 3:1 mixture of ammonium polyphosphate (APP) and pentaerythritol (PER).

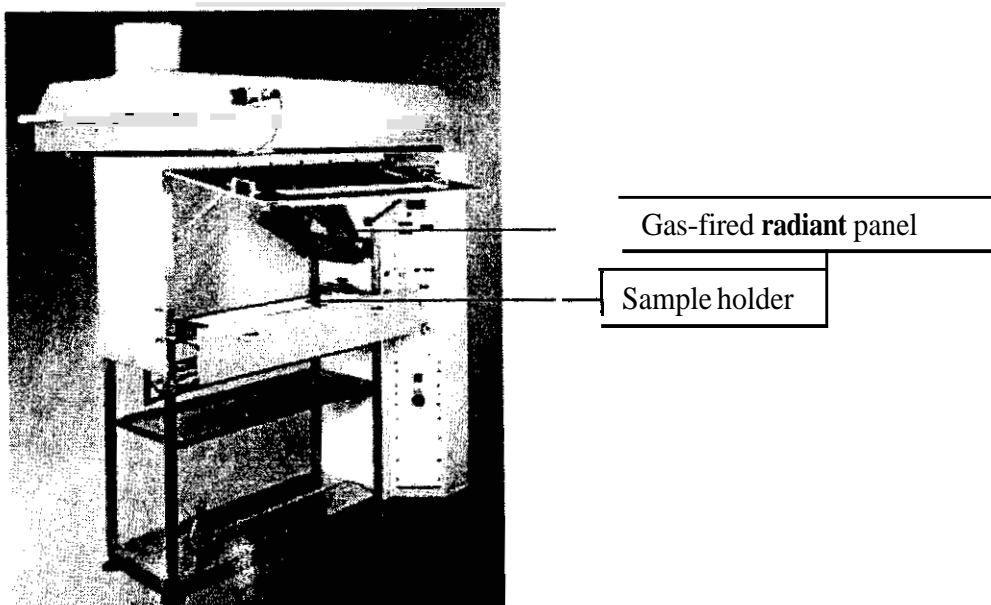


Figure 2. Flooring Radiant Panel apparatus

Results and Discussion

The approach we are pursuing focuses on the inherent high throughput capabilities of twin-screw extruders for rapid preparation of compounded samples (or libraries). The inherent **HT** nature of an extruder is derived from three important capabilities: 1) the **high** mass flow rates, 2) the ability to automate changes in the feeders used to deliver polymer and additive, 3) the ability to easily change the processing conditions, such **as** residence time and shear. While these attributes offer HT preparation of compounded nanocomposite samples, **they** also introduce a bottle-neck in our workflow: the characterization of the library. Nanocomposites present an especially difficult, albeit interesting, challenge in this regard. In contrast to conventional fillers and additives, where simple measurement of their concentration **might** suffice, characterization of nanocomposites must be done with resolution at the nano-scale. Specifically, one needs to determine the degree of mixing of the individual nano-scale particles. In addition, the effect of this nano-mixing on the overall order and morphology of the system must be determined. Traditionally this is done using transmission electron microscopy (TEM), X-ray diffraction (XRD) and other methods (small angle neutron scattering, (**SANS**), solid-state nuclear magnetic resonance (NMR), rheometry). These methods are not usually considered HT, although some have been converted to HT systems.¹⁹ Our recent efforts focus on removing this “characterization” bottleneck by using **in-line sensor** methods. We are developing two tools: 1) an optical sensor²⁰ and 2) a dielectric sensor.” Both sensors are directly in-line on the extruder. The details of these sensors will be published separately.

Once HT methods are in hand for preparing nanocomposite samples and for in-line characterization of them, the next task in the HT workflow is property characterization. Our interests in nanocomposites are focused on flammability and mechanical properties. The traditional approach to evaluating these properties often involves injection molding of test

coupons and property testing using standard procedures (tensile testing, dynamic mechanical analysis, flammability testing (UL 94 V, Cone Calorimeter, UL 910)). Instead we utilize the inherent HT nature of nanoindentation for mechanical properties measurements and new flammability characterization techniques developed involving measurement of flame spread, which take advantage of the *gradient* concept.

Workflow I- Extrusion and Flame Spread with Gradient Heat Flux

The extruder is an excellent tool for mass producing compounded polymer. Typical compounding of a formulated system involves setting the ratio of polymer feed-stock to additive at a fixed number, and then optimizing the processing conditions so as to extrude a consistent homogeneous product out the extruder's die, in the form of a strand or strip, which is subsequently chopped into pellets. In the first workflow described here the extruder is used ~~as~~ just described, to rapidly manufacture many constant composition (homogeneous) strips. Typical samples are shown in Figure 1.

When developing a HT method, standard samples with well characterized behavior are used first; and the results from the HT method are compared to that of the standard test method. A set of standard samples was made using polystyrene and a combination of additives (3:1 mixture of ammonium polyphosphate (**APP**) and pentaerythritol (PER)) that impart reduced flammability to the polymer. Bourbigot reports that PS formulated with a mass fraction of **29** % or greater of APP:PER (**3:1**) exhibits self-extinguishing properties.²³ The standard flammability test used for comparison is the Underwriters Laboratories 94 vertical test for electronic components (UL94).²³ This test is widely accepted, but because of the nature of the test it is not HT. In ~~an~~ attempt to develop a faster, more-reliable method to characterize the flammability properties of polymers we have used the *gradient* concept, but in somewhat of a different manner. Instead of building in

a compositional gradient in the sample, a gradient was used in the radiant flux environment that the homogeneous samples were exposed to (see Figure 3).

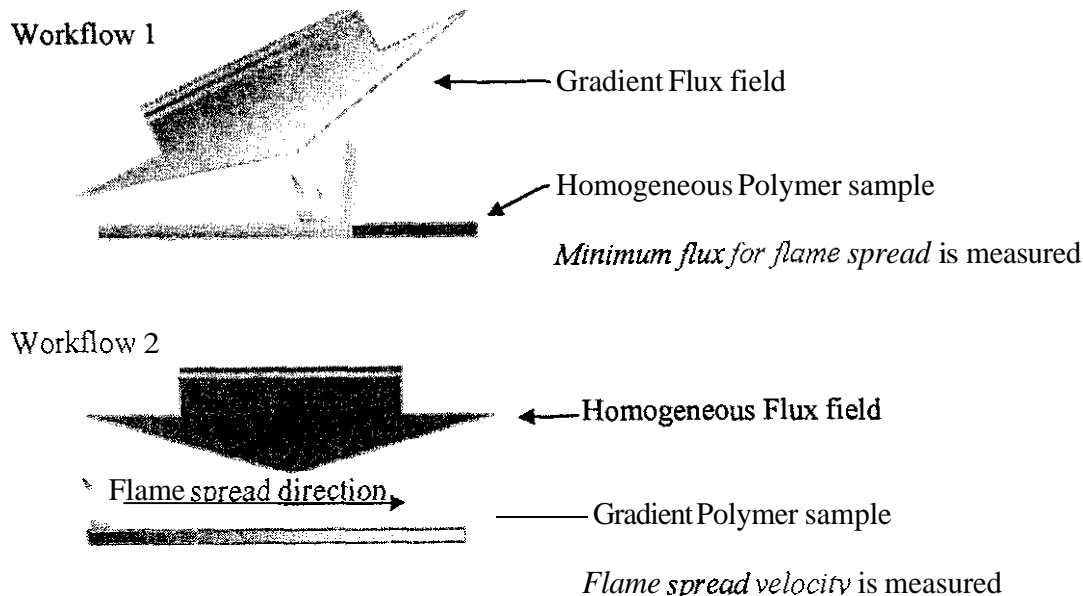


Figure 3. Schematic drawings of the two different flame spread approaches: one where the sample is homogenous and the flux field has a gradient in intensity (Workflow 1), and the other utilizing a compositional gradient within the sample and a homogenous flux field (Workflow 2).

The samples were burned under a gradient **flux** using a device similar to the standard Flooring Radiant Panel apparatus,²⁴ which is shown in Figure 2. This approach was designed in an attempt to develop a HT method which could be used to predict UL 94 test performance. The UL94 test is a pass-fail type test. The burning configuration is essentially upward flame spread. For the most common rating, V-0, the sample must self-extinguish in less **than** 10 s following each of two applications of a Bunsen burner flame (10 s application) to the sample. In upward flame spread, radiative heat transfer from the flame to the sample is the dominant heating mechanism, which drives the burning, however for small flames **as** in the UL94 test, convective heating dominates. The imposed flux in the radiant panel apparatus approximates *the* heat transfer in the UL 94V test, and both tests measure self-extinguishing behavior. However, by using a *flux gradient* this new approach can determine under what combination of conditions (imposed flux,

polymer type and flame retardant concentration) the sample will exhibit self-extinguishing behavior, but with only one set of experiments. A flux map in the region where the sample strips sit in the test apparatus is shown in Figure 4. Two to three samples were run at a time. The samples were ignited at the end, in the high-flux region (see Figure 5) and were allowed to bum until they self-extinguished. The bum length was converted to a minimum flux for flame spread, using the flux map. Typical data showed that samples with a higher concentration of flame retardant additive self-extinguished sooner, the bum length was shorter and the flux higher, than samples with lower flame retardant concentration. The repeatability of this HT flammability test is excellent ($2\sigma = 0.5 \text{ kW}$). The exact position where the sample self-extinguishes is determined during the experiment visually, or after by viewing the video of the experiment.²⁵ A video of a typical experiment, run on a single sample strip exposed to a flux gradient is shown in the imbedded digital video clip. Typical post-bum samples are shown in Figure 6.

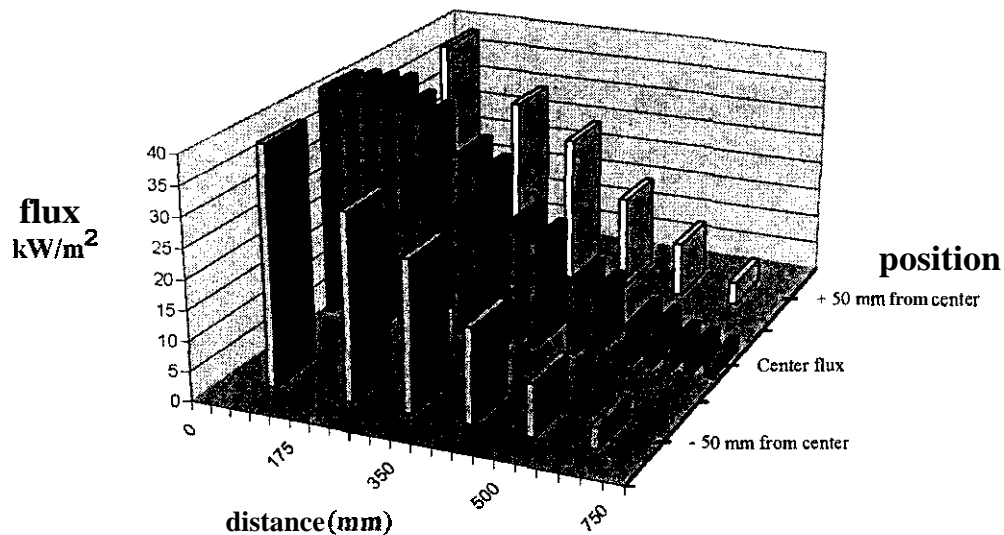


Figure 4. Flux gradient map in sample holder region of Radiant Panel apparatus.

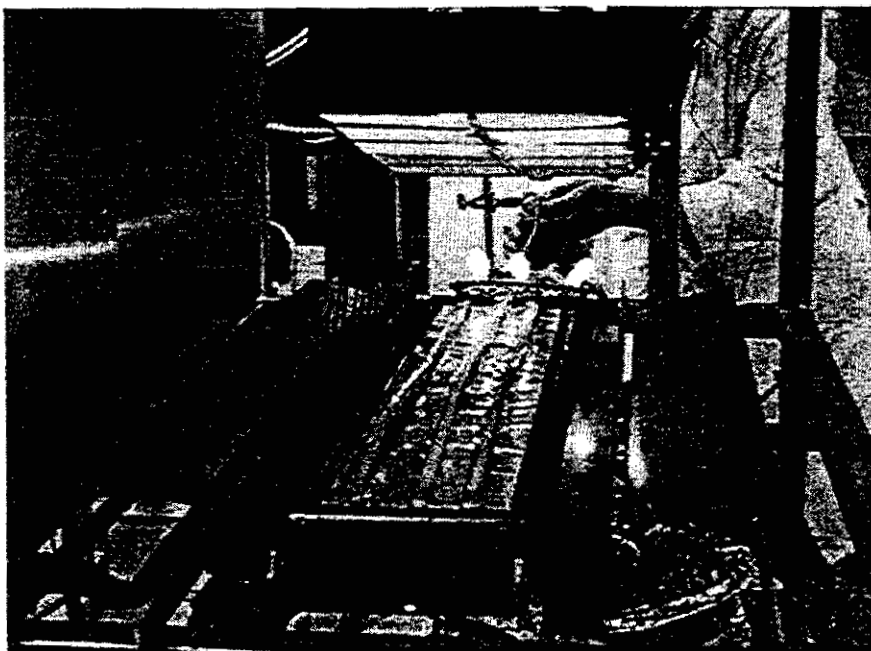


Figure 5. NIST Radiant Panel apparatus with 3 samples just prior to ignition.



Figure 6. Post-burn samples of extruded strips of polystyrene (PS) with various concentrations of a 3:1 mixture of ammonium polyphosphate (APP) and pentaerythritol (PER).

To evaluate the effectiveness of these two HT methods (sample extrusion and flame spread flammability screening) a library **was** designed **which** encompassed a wide range of combinations of an organo-layered-silicate additive (15A) and APP/PER flame retardant. Since

both of these additives are known individually to reduce the flammability of PS, we were interested in evaluating combinations for synergistic or antagonistic interactions.

The 38 formulations (4 replicates of each sample) were extruded in 2-3 days, and the flammability also characterized in only 2-3 days. The data are shown in Figure 7. Compared to the data generation rate for the UL94 V tests, this HT approach, Workflow 1, is 50-100 times faster. The same enhancement in datageneration rate is found when comparing this HT method's efficiency to characterizing the flammability of materials using the Cone Calorimeter. This faster method of evaluating many combinations of polymer, and additives reveals some interesting behavior for the systems studied. In the samples which contained only low mass fractions of either APPPER in PS (0%, 5%, and 10% (3:1) APP/PER in PS) or low mass fractions of organic modified layered silicate (2%, 4%, 6%, 8% and 10% OLS) we observed no self-extinguishing behavior. This was also the case for pure PS. However, introduction of 2% OLS into the 10% APP/PER /PS system enabled the sample to self-extinguish (sample labeled 10-2 in Figure 7). Synergistic behavior is observed for samples with of 2% OLS with 15 % and 20 % mass fractions of APP/PER (i.e., 15-2 and 20-2 in Figure 7). We define synergistic behavior as self-extinguishing behavior which falls above that for the pure APP/PER/PS, that is, above the red curve which connects the pure APP/PER/PS sample data.

15, 20, 25, and 30% (3:1) APP/PER in PS
 10% APP/PER with 2, 4, 6, 8, or 10% OLS in PS
 15% APP/PER with 2, 4, 6, 8, or 10% OLS in PS
 20% APP/PER with 2, 4, 6, 8, or 10% OLS in PS
 25% APP/PER with 2, 4, 6, 8, or 10% OLS in PS
 30% APP/PER with 2, 4, 6, 8, or 10% OLS in PS

0, 5, and 10% (3:1) APP/PER in PS
 2, 4, 6, 8, and 10% OLS in PS
Did not self extinguish

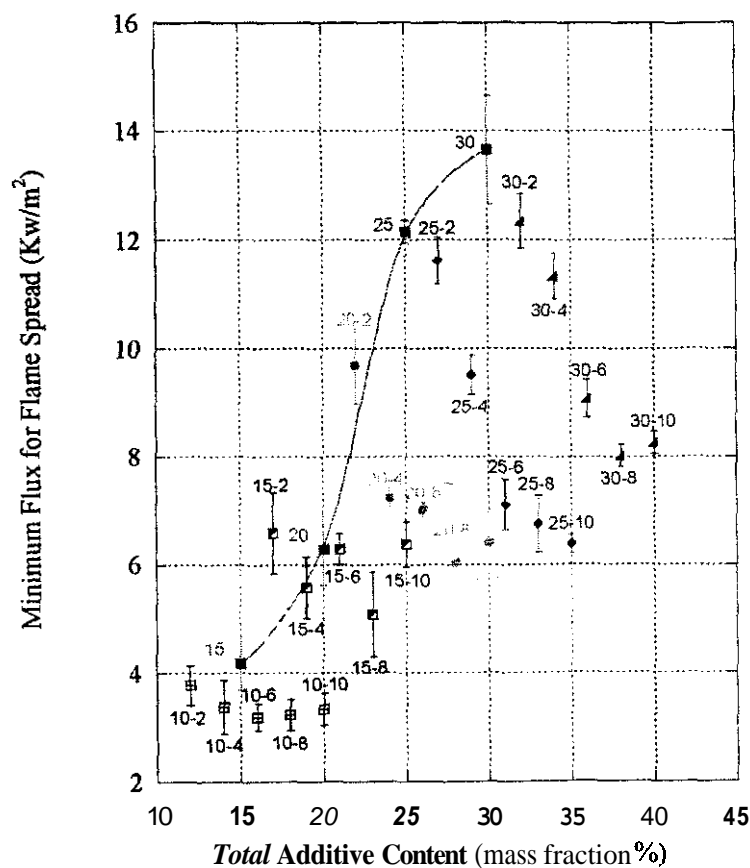


Figure 7. Plot of minimum flux for flame spread versus total additive content in PS samples.

For another subset of the library we observed "rule of mixtures" behavior, i.e., the data for combinations of the APP/PER and OLS falls very near the red curve. These combinations are 10-4, 10-6, 15-4, 15-6, 25-2 and 30-2 (in Figure 7). One might expect an overall better performance of both of these **sets** of samples (synergistic and rule-of-mixtures) if the effect of the OLS on the mechanical properties **was** included in the **evaluation**.²⁶ For all the other members of the library we observed antagonistic self-extinguishing behavior, i.e. the minimum flux for flame spread

was well below the red curve. These samples included 10-8, 10-10, 15-8, 15-10, 20-4, 20-6, 20-8, 20-10, 25-4, 25-6, 25-8, 25-10, 30-4, 30-6, 30-8, and 30-10. It appears (for the 20, 25 and 30 % APP/PER combinations) that as the mass fraction of OLS increased the minimum flux for flame spread decreased, linearly. We propose 3 possible mechanisms for this behavior: 1) OLS often raise melt viscosity and the APP/PER system is an intumescent foaming-charring system, which is very sensitive to melt viscosity; too high and the char does not foam, too low and the bubbles don't stay in the char. 2) Upon thermal decomposition (burning) the APP/PER produces phosphoric acid, which may undergo reaction with the basic OLS, essentially destroying the layered structure and reducing the effectiveness of the OLS.²⁷ 3) We have observed in other flammability experiments that OLS nanocomposites shorten the ignition time, e.g. in the Cone Calorimeter. We will return to this last issue in our discussion of the flame-spread test of gradient samples.

Workflow 2 – Extrusion and Flame Spread with Gradient Composition

As discussed above, the other new flammability characterization technique developed in our laboratories at NIST involves measurement of flame spread and takes advantage of the *gradient* concept.” In this approach we again take advantage of the inherent HT capabilities of the twin-screw extruder: 1) the high mass flow rates and 2) the ability to automate gradual changes in the feeders used to deliver polymer and additive. We evaluated two gradient systems: APP/PER in PS and OLS in PS. In this case we varied the ratio of additive to polymer over the extrusion experiment to prepare a compositional gradient within the extruded sample. A compositionally graded sample containing APP/PER in PS was produced in the extruder. In contrast to the flame spread test in Workflow 1 we did not use a gradient flux. Instead the samples are burned in our flooring radiant panel device under a *constant* flux of $(16.8 \pm 0.4) \text{ kW/m}^2$ (see Figure 3). From

the data in Figure 7 this incident **flux** is high enough to prevent self-extinguishing behavior, even for materials with very high concentrations. The sample **was** a strip (approximately 1.5m long, 7 mm wide and 2 mm thick) consisting of PS blended with varying amounts of the 3:1 APP/PER mixture. We attempted to create a linear concentration gradient (from $C = 0\%$ to $C = 30\%$ additive by mass) by increasing the rate of feed from the feeder containing the additive linearly with time.

The flame velocities were measured by pulling the extruded strip through a 300 mm heating zone such that the flame front remained at a fixed position. The results are plotted in Figure 8. The data (time, t) was collected at 0.050 m intervals, which were marked off on the sample holder strip, with the initial point (at $x = 0$) corresponding to the pure polymer ($C = 0\%$ at $x = 0$). The solid line **was** obtained **by** fitting the experimental data to a hypothetical function ($\Delta x \approx \frac{v_0}{b}(\exp(bt) - 1)$) that was derived by assuming a linear dependence between flame velocity (v) and additive concentration, which **was** also assumed to decrease linearly with distance. The validity of these assumptions is supported by the fact that this function does a good job of representing the experimental data. The derivative of the function ($v = v_0 \exp(bt) = bx + v_0$) in Figure 8 is a linear function of x (or of C , since $C = ax$) with a *negative* slope (b) indicating a reduction in the flame spread rate with increasing concentration of additive, as expected.

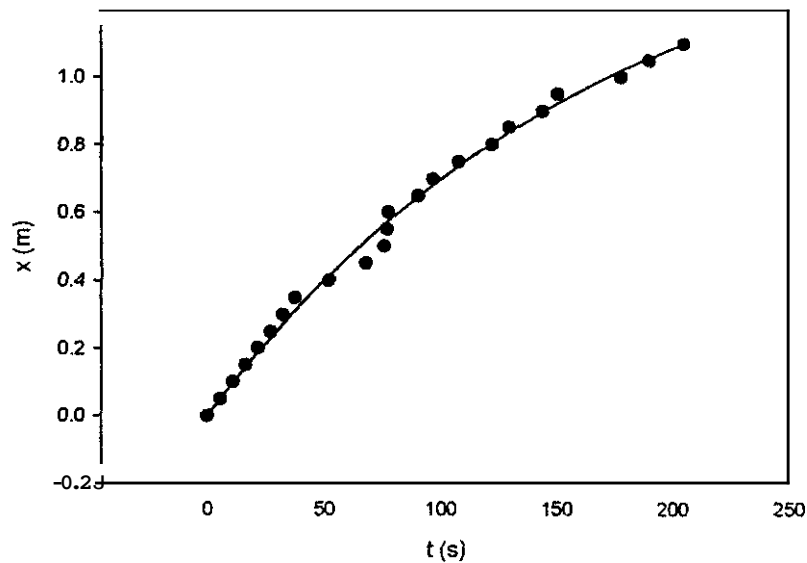


Figure 8. The progression of the flame front as a function of time measured for the APP/PER in PS gradient. The solid line was obtained by fitting the experimental data (circles) to a hypothetical function derived on the basis of assumptions stated in the text.

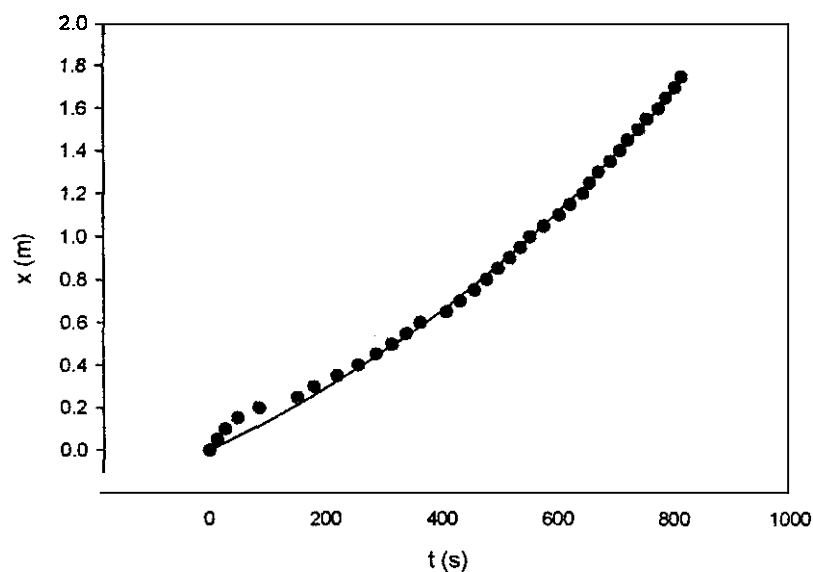


Figure 9. The progression of the flame front as a function of time measured for PS/OLS gradient. The solid line was obtained by fitting the experimental data (circles) to a hypothetical function derived on the basis of assumptions stated in the text.

Comparable data was collected for an OLS/PS gradient with an approximately linear concentration gradient of OLS varying from 0 % to about 14 % by mass. In this case, the flame

spread rate was *positive* ($0.95 \times 10^{-3} \text{ m/s} \pm 0.22 \times 10^{-3} \text{ m/s}$), i.e., the flame spread rate was observed to *accelerate* with increasing clay concentration (Figure 9). We propose the same explanation for this enhanced flame spread **as** mentioned above to explain the antagonistic behavior in some of the samples in Figure 7, i.e. that the shorter ignition times observed for *OLS* polymer nanocomposites, in Cone calorimetry experiments, may have a larger effect on the flame spread behavior than the effect of the reduced peak heat release rate (HRR). Tewarson has shown that indeed the ignition time is a more important parameter in upward flame spread models than the peak HRR.²⁹ Eventually, **we** would like to make simultaneous measurements of both flame spread rate and heat release rate to determine the optimal composition(s), which results in the best compromise between flame spread and HRR.

Conclusions

A HT method has been developed, which offers rapid preparation of nanocomposite and conventional-fillerpolymer libraries using twin-screw extrusion. This method allows preparation of homogeneous and gradient type samples. **A** HT method has also been developed for determining the flammability properties of the above polymer libraries. The flame spread measurements that are used to evaluate the flammability properties, take advantage of the gradient approach in two different manners. First, the homogeneous polymer samples are screened using a *flux gradient*. This determines under what combination of conditions (imposed flux, polymer type and flame retardant concentration) the sample will exhibit self-extinguishing behavior. Second, *gradient polymer samples* are screened using a constant flux. By combining these HT methods (extrusion and flame spread) the rate of data generation has been accelerated by at least 50 times! Furthermore, the structure-property relationships revealed in this work would not have been so easily *learned* without these HT approaches. **Work** is planned to combine

the *gradient flux* and a **series** of different homogeneous samples in a larger **flame** spread device so that **we** can have a compositional variation orthogonal to the **flux** gradient.

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(AFOSR- **ISSA-01-0001**).

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